

#### 5.1.4. ALTERNATIVE HALOCARBON MEASUREMENTS

Hydrochlorofluorocarbons (HCFCs) are important substitutes for CFCs in industrial applications. Their use will significantly shorten the time required for complete elimination of CFCs in industry [UNEP, 1991]. Although HCFCs contain chlorine, models indicate that they have a much reduced potential to deplete stratospheric ozone compared with CFCs. Ozone destruction capacity for HCFCs, as predicted by semi-empirical steady state ozone depletion potentials, ranges between 1 and 12% that of CFC-11 [WMO, 1991; Solomon *et al.*, 1992]. However, the ozone depletion potential for HCFCs over short periods, such as the next 5-10 years when chlorine is expected to reach a maximum in the stratosphere, is more accurately estimated with time-dependent ozone depletion potentials [Solomon and Albritton, 1992]. Because HCFCs have shorter atmospheric lifetimes than CFC-11, time-dependent depletion potentials can be as much as five times higher than steady-state ozone depletion potentials. For these reasons, and because of uncertainties concerning the chemistry and dynamics of the atmosphere, there is increasing concern over extensive use of HCFCs as replacements for CFCs. Some nations have accelerated the timetable for eliminating HCFCs earlier than recommended by the Copenhagen Amendments to the Montreal Protocol [UNEP, 1993]. Monitoring the global spatial and temporal variability of HCFCs is necessary for maintaining an accurate atmospheric chlorine inventory as

replacements gain acceptance in the marketplace and for validating model predictions concerning the fate of these compounds in the atmosphere [Prather and Spivakovsky, 1990].

Paired sample flasks filled at the four CMDL stations and three cooperative flask sampling locations during 1993 were analyzed in the Boulder laboratory using gas chromatography with mass spectrometric detection for HCFC-22, HCFC-142b, and HCFC-141b [Montzka *et al.*, 1993; 1994a, b]. Results for both HCFC-22 and HCFC-142b represent a continuation of measurements made in previous years. Before 1993, however, only preliminary mixing ratios were reported for HCFC-142b [Swanson *et al.*, 1993]. In addition to finalizing standardization for HCFC-142b, a consistent set of calibration standards was also prepared for HCFC-141b in 1993.

##### *Chlorodifluoromethane (HCFC-22)*

Measurements of the most abundant atmospheric HCFC continued in 1993 (Figure 5.8; Table 5.1). The latitudinally weighted global mean mixing ratio for HCFC-22 in mid-1993 was 106 ppt (Table 5.2). This is an increase of 4 ppt over the global mean determined for mid-1992 [Montzka *et al.*, 1993]. The growth rate for HCFC-22 from November 1991 through December 1993 is estimated at  $4.9 (\pm 1.0)$  ppt yr<sup>-1</sup>. The average difference between the northern and southern hemisphere during 1993 was  $13 \pm 1$  ppt.

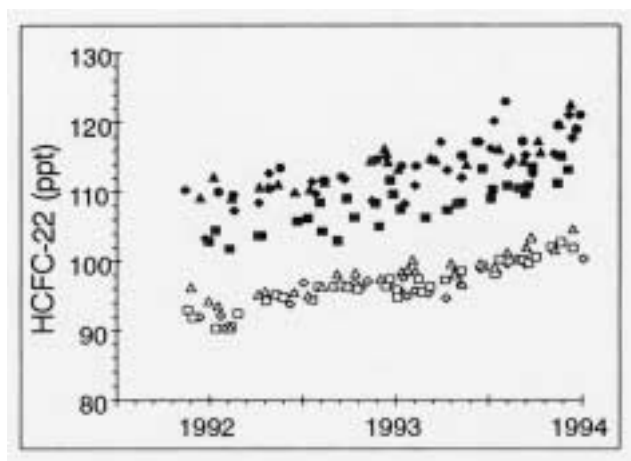


Fig. 5.8. Mixing ratios determined for HCFC-22 from air collected in flasks from seven different remote sampling locations: Alert, (•); BRW, (Δ); Niwot Ridge, (◆); MLO, (■); SMO, (△); CGO, (□); and SPO, (◇).

### 1-chloro-1,1-difluoroethane (HCFC-142b)

Hydrochlorofluorocarbon-142b is used predominantly as a substitute for CFC-12 in the fabrication of closed-cell foam [AFEAS, 1994]. It was also used to a lesser extent as an aerosol propellant and in refrigeration applications. The shift to HCFC-142b and away from CFC-12 for blowing foam began in 1988, and industry predicted that complete conversion would occur before the end of 1993 [UNEP, 1991].

The latitudinally-weighted global mean mixing ratio for HCFC-142b in mid-1993 was 4.3 ( $\pm 0.1$ ) ppt (Figure 5.9; Table 5.1 and 5.2). This is an increase of 1.0 ppt over the global mean determined for mid-1992. The growth rate for HCFC-142b over the entire sampling period (December 1991 through December 1993) is estimated at 1.1 ppt yr<sup>-1</sup>.

Mixing ratios determined for HCFC-142b during early 1992 in the northern hemisphere (Figure 5.9) are in reasonable agreement with those reported by *Schauffler et al.* [1993] from air collected in the upper troposphere

TABLE 5.1. CMDL Measurements of HCFCs from Flasks (1991-1993)

Station	Date	HCFC-22 (ppt)	HCFC-142b (ppt)	HCFC-141b (ppt)	Station	Date	HCFC-22 (ppt)	HCFC-142b (ppt)	HCFC-141b (ppt)
ALT	1991.871	110.2			BRW	1993.767	117.4	5.8	1.29
ALT	1992.052	110.0	3.6		BRW	1993.781	115.8	6.0	1.48
ALT	1992.128	109.5	3.8		BRW	1993.882	119.8	5.9	1.86
ALT	1992.328	110.5	4.3		BRW	1993.943	122.6	6.4	1.97
ALT	1992.385	113.4	4.1						
ALT	1992.620	111.5	4.1		CGO	1991.885	93.0		
ALT	1992.713	112.1	4.1		CGO	1991.910	91.9		
ALT	1992.907	114.7	5.0	0.55	CGO	1992.036	90.3	2.3	
ALT	1993.038	113.6	5.0	0.65	CGO	1992.115	90.6	2.4	
ALT	1993.112	113.7	5.4	0.70	CGO	1992.153	92.4	2.6	
ALT	1993.362	115.2	5.5	0.93	CGO	1992.306	94.2	2.2	
ALT	1993.438	117.2	5.7	0.87	CGO	1992.363	95.1	2.7	
ALT	1993.595	122.9		1.05	CGO	1992.402	94.8		
ALT	1993.688	117.2	5.6	1.51	CGO	1992.555	94.5	2.6	
ALT	1993.880	119.5	6.4	1.64	CGO	1992.587	96.2	2.7	
ALT	1993.975	119.0	6.8	1.99	CGO	1992.669	96.3	2.2	
ALT	1993.995	121.0	7.6	1.87	CGO	1992.705	96.6	2.4	
					CGO	1992.746	96.2	3.0	
BRW	1991.951	109.2			CGO	1992.798	96.0	2.9	
BRW	1992.022	112.2			CGO	1992.951	96.4*	3.3	0.23
BRW	1992.120	109.1	3.3		CGO	1992.970	97.4*	2.7	0.19
BRW	1992.268	110.7	3.8		CGO	1993.008	95.8	3.0	0.24
BRW	1992.372	111.2	3.3		CGO	1993.014	94.8	3.7	0.20
BRW	1992.459	110.0	4.1		CGO	1993.126	97.4	2.9	0.20
BRW	1992.538	110.4	3.5		CGO	1993.145	95.6	3.6	0.14
BRW	1992.618	111.4	4.2		CGO	1993.186	96.3	3.1	0.26
BRW	1992.866	114.5	4.8		CGO	1993.266	97.3	3.3	0.35
BRW	1992.940	116.3	5.3		CGO	1993.334	98.2	3.6	0.33
BRW	1992.959	114.3*	4.9	0.55	CGO	1993.356	98.6	3.4	0.35
BRW	1993.016	113.2	5.1	0.58	CGO	1993.471	99.2	3.7	0.34
BRW	1993.186	114.9	5.5	0.69	CGO	1993.537	98.2	3.6	0.34
BRW	1993.214	114.6	4.5	0.91	CGO	1993.564	100.3	4.0	0.43
BRW	1993.381	114.0	5.1	0.85	CGO	1993.608	99.9	3.7	0.46
BRW	1993.556	116.2	5.0	1.04	CGO	1993.669	100.2	3.3	0.45
BRW	1993.627	114.9	5.7	1.24	CGO	1993.688	100.2	3.5	0.45
BRW	1993.688	114.5	5.3	1.34	CGO	1993.718	99.8	3.8	0.42

TABLE 5.1. CMDL Measurements of HCFCs from Flasks (1991-1993)—Continued

Station	Date	HCFC-22 (ppt)	HCFC-142b (ppt)	HCFC-141b (ppt)	Station	Date	HCFC-22 (ppt)	HCFC-142b (ppt)	HCFC-141b (ppt)
CGO	1993.756	100.6	3.5	0.53					
CGO	1993.841	102.0	4.2	0.45	NWR	1993.606	114.1	5.2	1.35
CGO	1993.890	102.7	3.9	0.52	NWR	1993.701	115.4	5.5	1.63
CGO	1993.953	101.9	4.1	0.59	NWR	1993.740	112.6	5.3	1.29
					NWR	1993.855	115.5	5.9	1.69
MLO	1991.995	102.9			NWR	1993.932	121.1	6.1	1.98
MLO	1992.033	104.4	2.9		NWR	1993.951	117.8	5.9	1.88
MLO	1992.109	101.8	3.1						
MLO	1992.262	103.6	2.9		SMO	1991.901	96.2		
MLO	1992.281	103.6	3.2		SMO	1991.995	94.2		
MLO	1992.473	105.7	3.5		SMO	1992.046	93.6	2.4	
MLO	1992.530	106.1	3.6		SMO	1992.112	90.4	2.4	
MLO	1992.596	108.5	3.3		SMO	1992.262	95.2	2.5	
MLO	1992.607	104.3	3.0		SMO	1992.301	95.7	2.9	
MLO	1992.691	103.0	3.3		SMO	1992.456	95.5	2.8	
MLO	1992.740	109.1	5.0		SMO	1992.530	95.0	2.7	
MLO	1992.779	106.3	3.9		SMO	1992.607	96.3	3.3	
MLO	1992.893	108.4	4.0		SMO	1992.686	98.2	2.9	
MLO	1992.913	105.0	3.6		SMO	1992.784	98.3	3.8	
MLO	1992.970	111.6	4.6		SMO	1992.921	97.5		
MLO	1992.989	109.7*	4.6	0.41	SMO	1993.036	98.6	2.6	0.25
MLO	1993.027	107.5	3.8	0.41	SMO	1993.069	98.8	2.9	0.28
MLO	1993.162	106.3	3.9	0.53	SMO	1993.093	100.2	3.3	0.40
MLO	1993.280	107.4	4.2	0.66	SMO	1993.107	98.6	3.6	0.29
MLO	1993.334	108.2	4.8	0.71	SMO	1993.299	99.6	3.4	0.39
MLO	1993.353	108.4	4.2	0.70	SMO	1993.321	98.1	3.7	0.32
MLO	1993.469	113.3	4.9	0.91	SMO	1993.359	96.7	3.3	0.33
MLO	1993.515	109.1	4.5	0.87	SMO	1993.455	99.6	3.6	0.46
MLO	1993.526	110.4	4.8	0.71	SMO	1993.532	99.2	3.4	0.36
MLO	1993.603	110.9	5.6	1.02	SMO	1993.603	101.3	3.9	0.50
MLO	1993.660	110.6	4.9	1.17	SMO	1993.704	102.0	4.0	0.61
MLO	1993.699	109.8	4.7	1.13	SMO	1993.729	103.5	3.7	0.61
MLO	1993.718	111.0	4.8	1.20	SMO	1993.855	101.7	3.8	0.63
MLO	1993.737	113.6	5.1	1.10	SMO	1993.953	104.7	4.4	
MLO	1993.871	111.3	4.7	1.43					
MLO	1993.890	115.2	5.3	1.39	SPO	1991.948	92	2.1	
MLO	1993.929	113.2	5.1	1.39	SPO	1992.063	92.1	2.1	
					SPO	1992.079	90.3	2.1	
NWR	1991.978	103.3			SPO	1992.434	93.8	3.1	
NWR	1992.131	107.3	3.5		SPO	1992.506	96.9	2.7	
NWR	1992.265	108.4	3.4		SPO	1992.590	96.2	2.8	
NWR	1992.322	112.7	3.5		SPO	1992.694	96.4	2.8	
NWR	1992.552	111.5	4.0		SPO	1992.781	96.8	2.7	
NWR	1992.571	109.7	3.9		SPO	1992.817	96.2	2.5	
NWR	1992.609	111.7	3.6		SPO	1992.853	97.1	3.0	
NWR	1992.727	111.8	4.0		SPO	1993.022	95.7	3.0	0.24
NWR	1992.877	108.7	3.6		SPO	1993.044	97.6	3.1	0.25
NWR	1992.954	115.1	4.5	0.57	SPO	1993.066	94.9	2.9	0.28
NWR	1993.049	108.3	5.8	0.47	SPO	1993.104	95.7	3.6	0.20
NWR	1993.104	110.9	4.4	0.69	SPO	1993.181	95.4	2.9	
NWR	1993.244	117.2	6.0	1.00	SPO	1993.274	94.7	2.7	
NWR	1993.280	113.1	4.6	0.84	SPO	1993.353	96.6	3.3	0.36
NWR	1993.356	112.1	4.9	0.89	SPO	1993.458	98.9	3.2	0.30
NWR	1993.452	117.2	5.3	1.08	SPO	1993.545	98.4	3.5	0.38
NWR	1993.515	116.3	5.3	1.33	SPO	1993.603	99.7	3.0	0.37
NWR	1993.529	120.3	5.7		SPO	1993.701	99.6	3.6	0.31

\*Revised from that reported in Swanson *et al.* [1993]

TABLE 5.2. Estimates for Mid-Year Global Mean Mixing Ratios and Globally-Averaged Growth Rates

	1992 Mixing Ratios (ppt)	1993 Mixing Ratios (ppt)	All Data Growth Rates
HCFC-22	102	106	4.9 ppt yr <sup>-1</sup>
HCFC-142b	3.3	4.3	1.1 ppt yr <sup>-1</sup>
HCFC-141b	—	0.7	>100% yr <sup>-1</sup>

of the northern hemisphere (2.9-3.9 ppt, CMDL versus 2.1-3.4 ppt, NCAR) [Montzka *et al.*, 1994a]. Informal comparisons of gas standards prepared independently at these two laboratories were performed at CMDL and indicate that the standards agree to within 5%.

When compared with levels calculated from emission estimates [AFEAS, 1994] and a finite-increment model, the results from both laboratories are 1.5-1.8 times (or 1.3-1.5 ppt) greater than expected [Montzka *et al.*, 1994a]. Although the reasons for this discrepancy are unclear at present, it is not likely that this difference results from inaccurate estimates of atmospheric lifetime for HCFC-142b. HCFC-142b has been emitted into the atmosphere for only a short period of time relative to its predicted atmospheric lifetime and, therefore, model calculations performed with a much longer lifetime than 20 years (100-1000 years) do not remove the discrepancy between observations and model results based on available emission estimates.

#### 1,1-dichloro-1-fluoroethane (HCFC-141b)

HCFC-141b is currently used as a CFC-11 substitute for blowing closed-cell foams and as a substitute for CFC-113 as a solvent and cleansing agent. Unlike HCFC-142b, HCFC-141b was not commercially available until the beginning of 1993 when toxicological

studies were scheduled to be completed [UNEP, 1991]. Before 1993, many companies in the foam sector stated their intention to eliminate CFC-11 for this use during that year [UNEP, 1993; EPA, 1993]. While substitution of CFC-113 with HCFC-141b is also likely to occur rapidly, industry experts estimate that only ~5% of past demand for CFC-113 will be satisfied with HCFCs owing to the many alternative processes and approaches that were developed by industry to reduce the amount of CFC-113 needed in these applications [UNEP, 1991].

The latitudinally-weighted global mean mixing ratio for HCFC-141b in mid-1993 was 0.7 ( $\pm 0.1$ ) ppt (Figure 5.10; Table 5.1 and 5.2) [Montzka *et al.*, 1994a]. The global mean mixing ratio increased exponentially during 1993, at greater than 100% yr<sup>-1</sup>. The rapid increase in ambient mixing ratio during 1993 is likely the result of a dramatic shift towards use of HCFC-141b in industrial applications after toxicological studies were completed.

Recently, Schauffler *et al.* [1995] reported mixing ratios for HCFC-141b from samples collected during a number of cruises in the Pacific, Southern, and Arctic Oceans over the past 2 years. A comparison of mixing ratios determined from samples collected at similar times and at similar latitudes, reveals that results from the two independent laboratories agree to within 0.1 ppt [Schauffler *et al.*, 1995].

#### Stability of HCFCs in Flasks

Because measurements are based on the analysis of air contained within flasks that were filled at an earlier date, it is necessary to ensure that these compounds are stable within these containers over time before reliable and accurate mixing ratios can be reported. The potential for production and/or loss of HCFC-22, -142b, and -141b within sample flasks is investigated here by: (1) reanalyzing air within a flask after a period of time

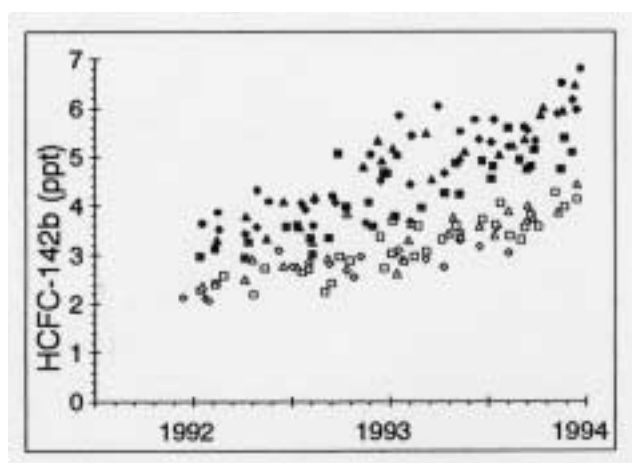


Fig. 5.9. Mixing ratios determined for HCFC-142b from air collected in flasks from seven different remote sampling locations: Alert, (•); BRW, (Δ); Niwot Ridge, (◆); MLO, (■); SMO, (Δ); CGO, (□); and SPO, (◇).

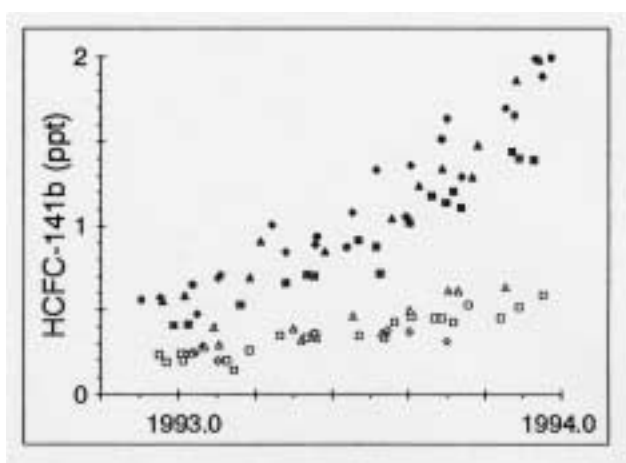


Fig. 5.10. Mixing ratios determined for HCFC-141b from air collected in flasks from seven different remote sampling locations: Alert, (•); BRW, (Δ); Niwot Ridge, (◆); MLO, (■); SMO, (Δ); CGO, (□); and SPO, (◇).

has elapsed to see if consistent results are obtained; (2) determining if relationships between the amount of time the air is stored in a flask and reported mixing ratios are apparent; (3) determining if differences attributable to humidity levels within a flask are apparent in results from SPO and CGO; and (4) determining if disagreements in HCFC mixing ratios within simultaneously filled flasks are significant relative to the precision of the analysis.

After they were received in Boulder, selected flasks were analyzed two or more times to study the effects of storage time on different compounds within flasks (Figure 5.11). Results from the two analyses are compared with the variability observed for duplicate injections of air from flasks that were collected in 1992 and 1993. For more than 90% of the flasks that were reanalyzed, the results obtained for all three HCFCs were within the 95% confidence interval for variability observed for duplicate injections of air from flasks. The larger differences observed for HCFC-141b and -142b upon reanalysis are associated with the initial stages of the measurement program when mixing ratios and signal-to-noise ratios were exceptionally low.

Although the second analysis was usually performed under identical instrumental conditions, a more polar, chromatographic column was sometimes used (Figure 5.11). In the chromatographic analysis of complex environmental samples, it is useful to compare results obtained under different instrumental conditions to ensure that these results are independent of the conditions chosen. Analysis of air samples with capillary columns having different polarity allows for an estimate of the importance of coeluting compounds on the results obtained for atmospheric HCFCs using this chromatographic instrument. For all three HCFCs, results obtained during reanalysis with the more polar column were not significantly different from the initial analysis. Because it is unlikely that a compound would interfere consistently under different instrumental conditions, these results suggest that measurements of these HCFCs are free of these types of interferences.

Flask samples sent from the stations in 1991, 1992, and 1993 (excluding SPO) were analyzed at the CMDL Boulder laboratories anywhere from 2 to 76 days after they were collected (mean = 24 days; median = 22 days). These delays result from shipping and instrument availability. Longer delays are associated with samples collected at SPO because no shipments leave this site during the southern hemisphere winter. To ascertain if these delays adversely affect HCFC measurements, residuals from loess fits to the data obtained at each station are compared with the time elapsed between sampling and analysis of each flask (Figure 5.12). A loess smoothing fraction of 0.3 was used to generate the residuals plotted in this figure to remove variability associated with seasonality and non-linear growth rates but retain short-term variability. No significant

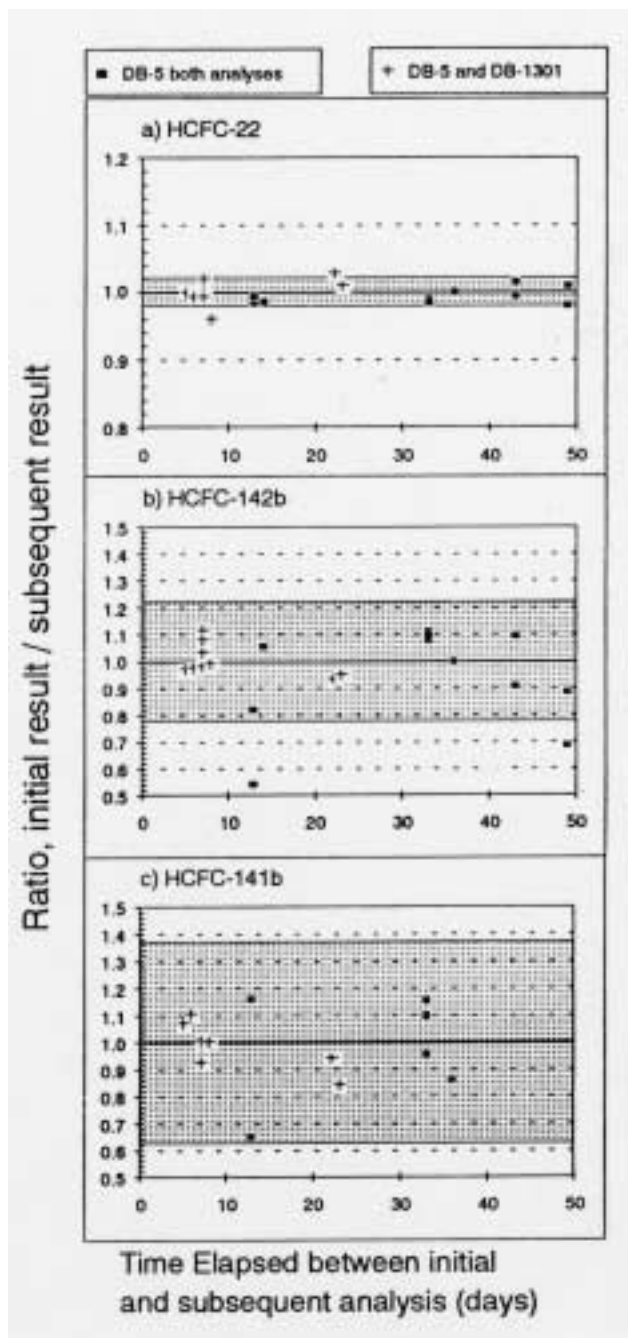


Fig. 5.11. Results obtained when air within samples flasks was re-analyzed after a period of time had elapsed for (a) HCFC-22, (b) HCFC-142b, and (c) HCFC-141b. Squares represent re-analyses that were performed under identical instrumental conditions. Plus symbols (+) represent results from re-analyses that were performed with a more polar analytical column (DB-1301 versus DB-5). The shaded area represents 2 times 95% of the range of variability observed for duplicate injections of air from all flasks collected in 1992 and 1993.

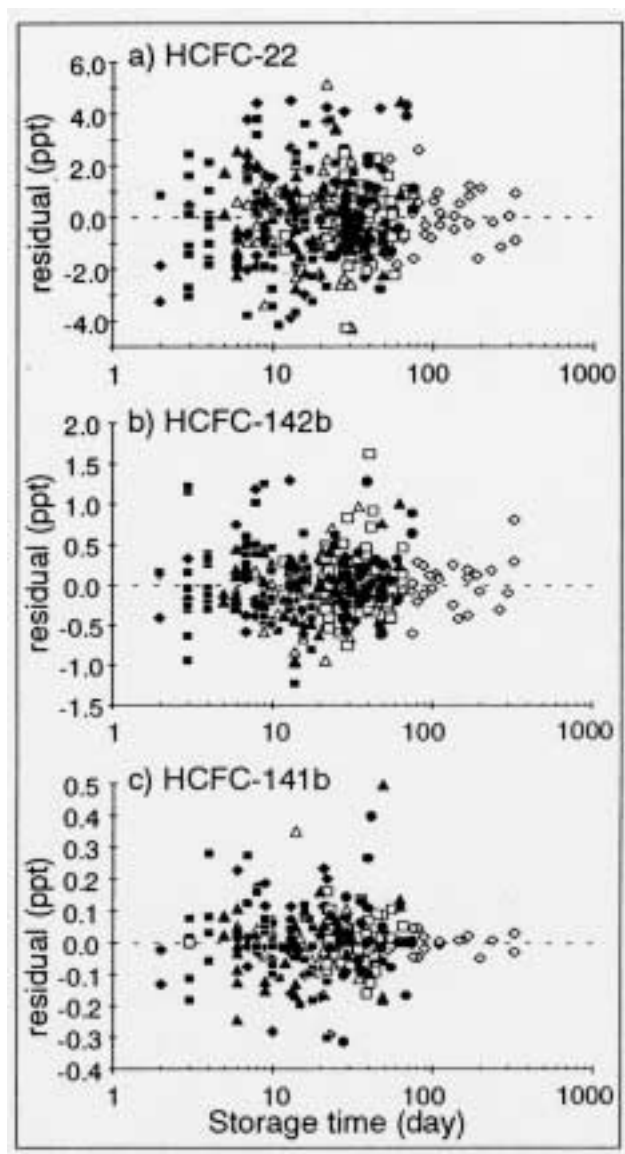


Fig. 5.12. Residuals from loess fits to flask data obtained over time are plotted against elapsed time between flask collection and analysis for (a) HCFC-22, (b) HCFC-142b, and (c) HCFC-141b. Symbols represent the different sampling stations (see Figure 5.8). The loess fits are performed for each compound at each sampling station with a smoothing fraction of 0.3.

relationship between storage time and residual is observed, and scatter in the residual does not increase at longer storage times. Although the scatter observed in Figure 5.12 represents an upper limit for the magnitude of problems associated with sample storage in these flasks under a wide range of sample humidities, it also encompasses variability associated with the atmosphere and instrumental analysis.

The effect of humidity on mixing ratios for HCFCs within flasks can be investigated by comparing data from SPO with the results obtained at CGO. For compounds emitted predominantly in the northern hemisphere, and for which atmospheric growth and loss rates are small when compared with intrahemispheric mixing rates, similar mixing ratios are observed at SPO and CGO [Steele *et al.*, 1987; Elkins *et al.*, 1993]. Ambient conditions at these two locations, however, are significantly different; while air collected at SPO can be extremely dry, air is sampled from within the marine boundary layer at CGO and ambient temperatures are, on average,  $\sim 60^\circ\text{C}$  higher. Losses of certain compounds such as  $\text{CCl}_4$  within electropolished stainless-steel flasks are known to be dependent upon the amount of water in a flask [Schauffler *et al.*, 1993; Montzka *et al.*, 1994b]. Despite large losses of  $\text{CCl}_4$  within a number of flasks filled at SPO, ambient mixing ratios for HCFC-22 and HCFC-142b are very similar at both of these stations (Figure 5.13). These results suggest that within the range of humidities encountered at these two stations, mixing ratios determined for these HCFCs are independent of the amount of water present within these flasks [Montzka *et al.*, 1994b].

Based on the majority of measurements made for HCFC-141b in flasks collected at SPO, a similar conclusion can be drawn for this HCFC. However, in three flasks it appears as if mixing ratios from SPO are low relative to the measurements made concurrently at CGO. While this suggests that HCFC-141b may undergo losses within extremely dry flasks, rather large uncertainties are associated with these measurements owing to the extremely low mixing ratios of this compound in the southern hemisphere during early 1993. Furthermore, observed differences between mixing ratios determined for HCFC-141b within flasks collected at SPO and CGO are not correlated with carbon tetrachloride losses in these flasks, suggesting that the characteristics of a flask that cause losses of carbon tetrachloride do not affect mixing ratios determined for HCFC-141b.

Results from the flask measurement program are based on flask pairs collected simultaneously and in a parallel flow arrangement. During analysis, each flask is treated independently, and the results obtained are averaged to arrive at a best estimate for ambient air mixing ratios at the time the flask was filled. Results obtained for compounds within simultaneously filled flasks should agree to within the analytical precision of the instrument. Disagreements between mixing ratios determined within flasks that are filled in parallel can indicate problems associated with filling flasks, flask cleanliness, and compound integrity within flasks.

For all three HCFCs, the median difference observed between simultaneously filled flasks is similar to the median uncertainty associated with repetitive injections of air from a single flask (Figure 5.14). Furthermore, the entire distribution of flask-pair differences are

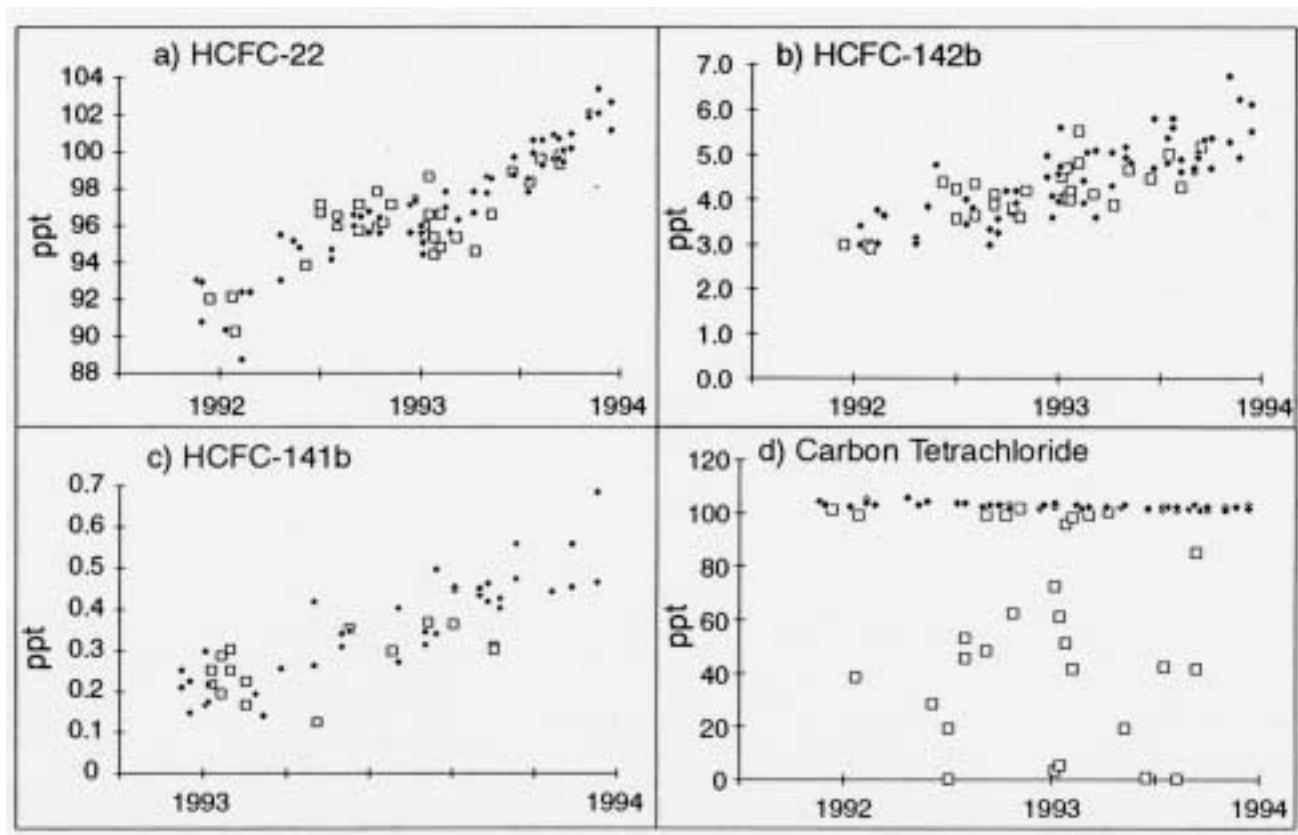


Fig. 5.13. Mixing ratios observed within individual flasks for different HCFCs at both CGO (♦) and SPO (□) for (a) HCFC-22, (b) HCFC-142b, (c) HCFC-141b, and (d)  $\text{CCl}_4$ .

similar to, if not lower than, observed analysis standard deviations for all three HCFCs, and this suggests that no measurable differences are observed in flasks filled simultaneously at the sampling stations. For HCFC-22, however, there are instances where values obtained from simultaneously filled flasks disagree significantly ( $\leq 5\%$  occurrence for disagreements greater than 3 ppt). Sample pairs with such large differences are not used when calculating atmospheric growth rates or global background mixing ratios [Montzka *et al.*, 1993]. In the discussion above, it was concluded that HCFC-22 is stable within flask canisters for extended periods under widely differing ambient water mixing ratios and, therefore, it is difficult to explain these larger differences based on the instability of HCFC-22 within flasks. A more likely cause for these larger differences rests with problems associated with filling flasks or flask cleanliness. Separate analyses have shown that levels of HCFC-22 are typically 100-1000 times higher in laboratory air than in ambient air at remote sampling locations (S. Montzka, unpublished data).

Occasional problems with small leaks or insufficient purging of flasks either during filling or analysis could generate the type of result observed.

#### **Measurement of Additional Chlorinated Compounds with GC-MS Instrumentation**

The versatility of the GC-MS technique allows for the detection of many different compounds within a single chromatogram. In addition to the compounds already quantified with GC-MS during a single analysis of air from flasks (HCFCs, CFCs, halons, methyl halides, methyl chloroform, and carbon tetrachloride), monitoring of several more chlorinated compounds began in 1993. Mixing ratios for methyl chloride ( $\text{CH}_3\text{Cl}$ ), dichloro-methane ( $\text{CH}_2\text{Cl}_2$ ), chloroform ( $\text{CHCl}_3$ ), and tetrachloro-ethylene ( $\text{C}_2\text{Cl}_4$ ) were determined for air contained within flasks. Measurements of these additional compounds are performed by monitoring ions unique to these chlorinated hydrocarbons at predetermined elution times. No additional changes to the experimental technique are required. Preliminary results for these compounds are presented in Figure 5.15.

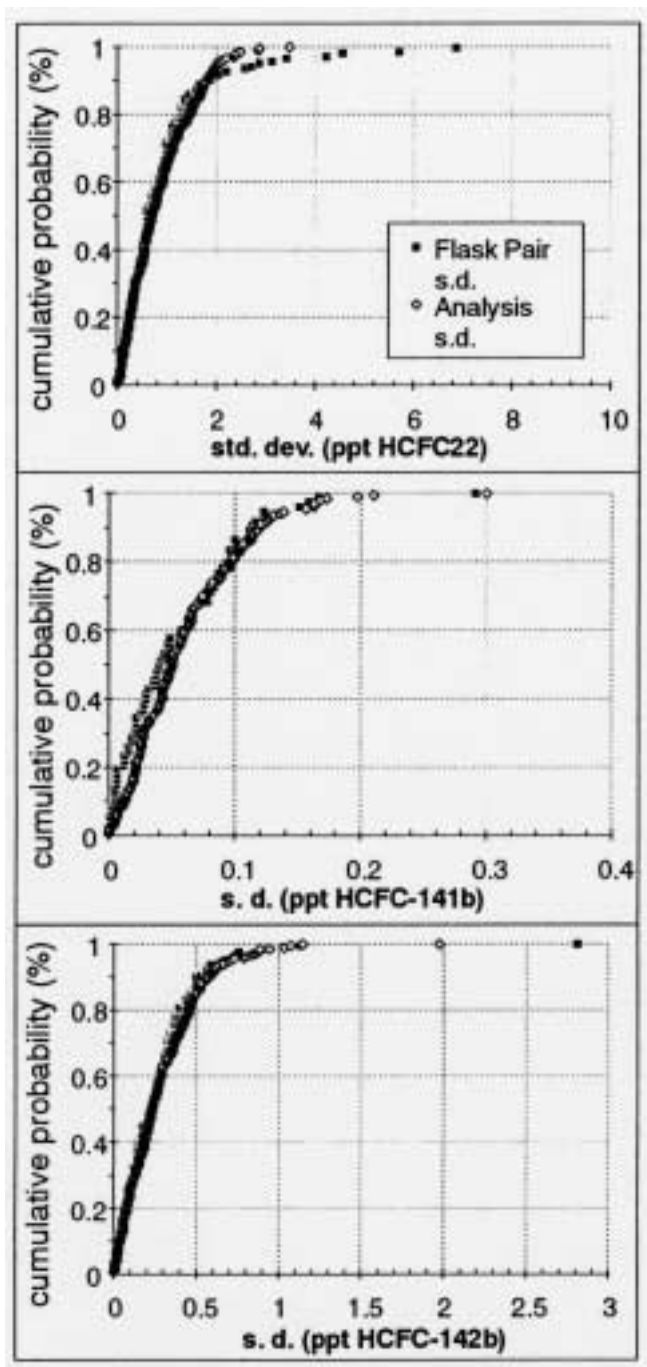


Fig. 5.14. Standard deviations obtained for duplicate injections of air from individual flasks (analysis s.d.) plotted on a cumulative probability scale. Also shown are the differences measured in simultaneously filled flasks (pair standard deviations). The data presented are for all samples collected and analyzed through the end of 1993.

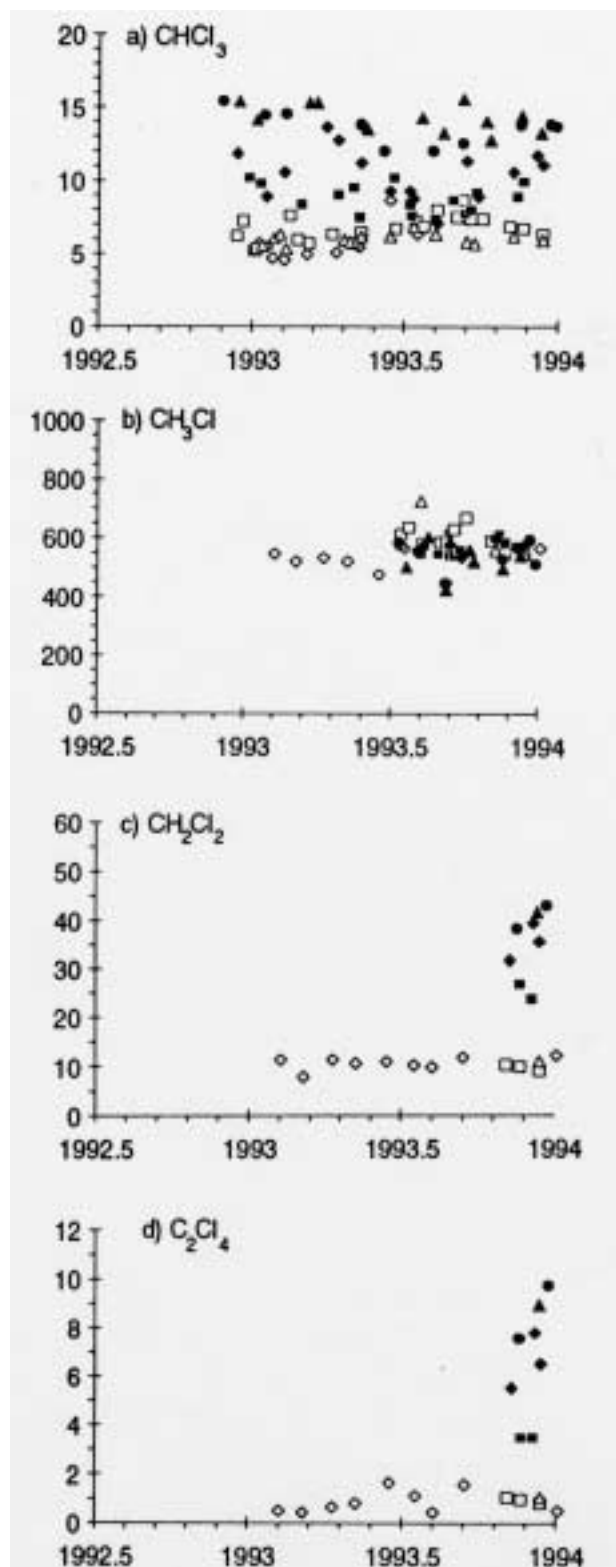


Fig. 5.15. Mixing ratios determined for different chlorinated compounds from air collected in flasks at seven different remote sampling stations. Symbols are identical to those in Figure 5.8. Mixing ratios for compounds other than  $\text{CH}_3\text{Cl}$  are reported relative to a preliminary calibration scale.